

## HIGH EXPANSION DENTAL ALLOYS

### CROSS-REFERENCE TO RELATED APPLICATIONS

This is application claims priority to U.S. Provisional Application No. 60/224,306  
5 filed August 10, 2000 and U.S. Provisional Application No. 60/275,539 filed March 13, 2001  
which are incorporated herein by reference.

### FIELD OF THE INVENTION

This invention relates to high expansion cobalt-chrome-based dental alloys.

### BACKGROUND OF THE INVENTION

Gold-based alloys in dentistry were initially replaced by more economical palladium-  
based alloys. Recent increases in the price of palladium are making these alloys very  
expensive. Other economical alternatives have been nickel-based, cobalt-based and titanium-  
15 based systems. Nickel-based alloys allegedly have sensitivity and toxicity concerns.  
Titanium-based alloys are difficult to process and require special care and expensive  
equipment. These alloys, while being thermally compatible with conventional porcelains are  
not compatible with many high expansion porcelains available today. Although gold-based  
alloys are being marketed for use with high expansion porcelains, no economical alternatives  
20 exist. Metal free ceramic/composite systems and sintered or plated copings have also been  
used, but may lack the strength and other properties inherent in metals and alloys which  
render metals and alloys more desirable than their ceramic counterparts.

Thus, there is need for developing non-allergenic cobalt-based alloys to fill this void  
that exhibit many of the properties of precious metal alloys heretofore considered desirable in  
25 the fabrication of porcelain-veneered bridgework and crowns.

## SUMMARY OF THE INVENTION

These and other objects and advantages are accomplished by the present invention which provides chromium-cobalt alloys which are significantly different from chromium-cobalt alloys heretofore employed in the fabrication of prosthetic dental appliances. The alloys herein exhibit greatly improved oxidation resistance thereby facilitating the formation of a tenacious bond with high-expansion porcelain. The alloys herein comprise cobalt, chromium and manganese as essential components and include one or more of aluminum, indium, gallium, tin, and germanium, and may include one or more of iron, nickel, palladium and platinum. Optional components include gold, tantalum, niobium, molybdenum, tungsten, vanadium, iridium, ruthenium, rhenium, titanium, silicon, copper, zirconium, hafnium, boron, yttrium, and rare earths metals. The alloys herein are useful with high-expansion dental ceramics and porcelains, most preferably with those recently introduced to the market in the range of about range from 14 to  $18.5 \times 10^{-6}$ .

## DESCRIPTION OF THE INVENTION

The cobalt-chromium alloys of the present invention are especially suited for use in the fabrication of prosthetic dental appliances since the cobalt in the alloy imparts characteristics to the alloy which closely correspond to those of alloys having a high precious metal content. Cobalt is the major component, imparting to the alloy its inherent corrosion and tarnish resistance. The chromium in the alloy enhances this resistance. Chromium also acts as a solid solution strengthener and provides a convenient means of adjusting the thermal expansion characteristics of the alloy to conform to the variations encountered upon use of different commercial porcelains.

The cobalt-chromium alloys of the present invention comprise the following ranges of components as set forth in Table 1 below.

Table 1

ELEMENTS	RANGE (WT%)	PREFERRED RANGE
Cobalt	about 60- about 85	about 65- about 80
Chromium	about 15- about 30	about 18- about 25
Manganese	about 2- about 20	about 2- about 10
Iron, Nickel, Palladium, or Platinum, or mixture thereof	about 1- about 20	about 2- about 10
Aluminum, Indium, Gallium, Tin, or Germanium, or mixture thereof	about 1- about 15	about 1- about 7
Gold	0- about 10	about 1- about 5
Tantalum, Niobium, Molybdenum, Tungsten, or Vanadium, or mixture thereof	0- about 15	0- about 5
Iridium, Ruthenium, Rhenium, Titanium, Silicon, or Copper, or mixture thereof	0- about 6	about 0.1- about 3
Zirconium, Hafnium, Boron, Yttrium, or rare earths metals, or mixture thereof	0- about 5	0- about 1

The addition of one or more of manganese, aluminum, indium, gallium, tin, germanium has been found to increase the coefficient of thermal expansion and lower the melting temperature of the alloy. Manganese is an important component in the alloy because it is most effective in raising the coefficient of thermal expansion without embrittling the alloy, it acts as a desulfurizing agent and improves the castability of the alloy. It is preferable that manganese and aluminum are present in an amount equal to or greater than about 2%. Aluminum also improves the oxidation resistance of the alloy.

It has been found that one or more of zirconium, hafnium, boron, yttrium, and rare earths metals may be added to the alloy to function to fill lattice discontinuities that may exist at grain boundaries and thereby increase structural perfection.

The following examples in Table 2 further illustrate the criticalities of the alloy composition of the present invention. All percentages and parts are by weight.

Table 2

Elements	Alloy 1	Alloy 2	Alloy 3	Alloy 4	Alloy 5	Alloy 6	Alloy 7	Alloy 8	Alloy 9
Gold	0	2	0	0	0	0	0	0	0
Platinum	0	0	0	0	0	2	0	0	0
Cobalt	64	66	69.9	69.5	61	64	66	64	64
Chromium	20	20	20	20	25	20	20	20	20
Manganese	4	6	6	5	6	6	6	6	6
Aluminum	2	2	4	4	2	2	2	2	2
Gallium	6.5	4	0	0	6	6	6	6	6
Molybdenum	3.5	0	0	0	0	0	0	0	0
Tungsten	0	0	0	0	0	0	0	0	0
Indium	0	0	0	0	0	0	0	0	0
Silicon	0	0	0	0.9	0	0	0	0	0
Zirconium	0	0	0	0	0	0	0	0	0
Yttrium	0	0	0.1	0.1	0	0	0	0	0
Ruthenium	0	0	0	0.5	0	0	0	0	0
Tantalum	0	0	0	0	0	0	0	0	0
Palladium	0	0	0	0	0	0	0	2	0
Iridium	0	0	0	0	0	0	0	0	2
Total	100	100	100	100	100	100	100	100	100

- 5 The thermal expansion properties of the alloys of Table 2 are provided in Table 3 below along with mechanical and other properties for alloys 2 and 7.

Table 3

Properties	Alloy 1	Alloy 2	Alloy 3	Alloy 4	Alloy 5	Alloy 6	Alloy 7	Alloy8	Alloy 9
CTE (x 10- 6/°C) (25-500°C)	16.22	16.78	16.52	16.46	16.18	16.68	16.9	16.75	16.63
Yield Strength MPa	—	281	—	—	—	—	274	—	—
Ultimate Tensile Strength MPa	—	447	—	—	—	—	422	—	—
Hardness, HV <sub>5</sub>	—	227	—	—	—	—	225	—	—
Melting Range °C	—	1270 - 1365	—	—	—	—	1240- 1375	—	—

The alloys of the present invention exhibit a melting range of from about 900 °C to about 1400 °C, and preferably from about 1000 °C to about 1350 °C and a coefficient of thermal expansion in the range of about 14.5 to about 19 x 10<sup>-6</sup>/°C at about room temperature to about 500°C, and more preferably at about 15 to about 18 x 10<sup>-6</sup>/°C at about room temperature to about 500°C. It is important that the thermal expansion is slightly higher than that of the porcelains currently available, thereby placing the porcelain under compression and minimizing stress at the interface. The thermal expansion of the alloys herein indicate that the alloys are suitable for use with high-expansion porcelains such as OPC® Low Wear™ porcelain (Jeneric®/Pentron® Incorporated) and Golden Gate porcelain (Ducera). The solidus temperature is preferably above about 800°C and the liquidus is below about 1500°C. The most preferred melting range is 1000-1350°C.

The yield strength of the alloys herein is in excess of about 250 MPa; the tensile strength is in excess of about 400 MPa; and the elongation is in excess of about 3%. The Vickers Hardness of the alloy is no greater than about 400 HV<sub>5</sub> and preferably no greater than about 250 HV<sub>5</sub>. Lower hardness imparts working characteristics similar to white precious

metal alloys. The tests performed on the alloys and the properties of the alloys follow guidelines as per ISO 9693.

The alloys herein can be prepared by conventional alloying techniques. If desired, alloying can be effected in air, under vacuum or by employing a blanket of inert gas such as argon. The latter precautions, although preferred, are not considered essential. Generally, the major alloy constituents are melted first, such as through use of an induction furnace, taking care to maintain a homogeneous distribution of chromium in the melt by overcoming its tendency to float to the surface. After the cobalt and chromium have been melted and are well dispersed, the manganese can be added. Thereafter, the remaining alloy constituents can be added in either elemental form or as a preformed alloy with cobalt or chromium. Once the alloy melt is prepared and ingots cast therefrom, the remelting of the alloy ingot may be accomplished using a standard natural gas/oxygen torch or induction melting equipment.

The alloys herein are useful in the manufacture of dental restoratives including, but limited to, crowns, bridges, space maintainers, tooth replacement appliances, orthodontic retainers, dentures, posts, jackets, inlays, onlays, facings, veneers, facets, implants, abutments, splints, partial crowns, teeth, cylinders, pins, and connectors. Preferably the alloys herein are used as the core material and may be veneered with ceramic or porcelain materials, such as high-expansion porcelains.

While various descriptions of the present invention are described above, it should be understood that the various features can be used singly or in any combination thereof. Therefore, this invention is not to be limited to only the specifically preferred embodiments depicted herein.

Further, it should be understood that variations and modifications within the spirit and scope of the invention may occur to those skilled in the art to which the invention pertains. Accordingly, all expedient modifications readily attainable by one versed in the art from the disclosure set forth herein that are within the scope and spirit of the present invention are to be included as further embodiments of the present invention. The scope of the present invention is accordingly defined as set forth in the appended claims.